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LOW TEMPERATURE PULSED PLASMA DEPOSITION

PART 3 : A METHOD OF DEPOSITION OF ALUMINIUM AND TIN  
AT ROOM TEMPERATURE

by

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Low Temperature Pulsed Plasma Deposition Part 3:

A Method for the Deposition of Aluminium and Tin at Room Temperature

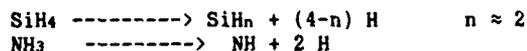
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ABSTRACT

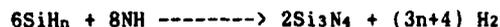
A method is described for the room temperature deposition of tin and aluminium films using the recently published pulsed plasma deposition technique. It is shown that high powered pulsed discharges of organometallics generally produce metal carbides, but by using pulsed discharges of hydrogen between the deposition pulses, virtually all the carbon in the film can be removed without requiring substrate heating. The technique is found to be capable of producing metal films at moderate deposition rates and of quality close to that of sputtered and evaporated films, but at temperatures close to room temperature. Results are presented on the conductivity of the films and practical applications for this technique are discussed.

INTRODUCTION

Plasma enhanced chemical vapour deposition (PECVD) is a widely-used technique in the production of amorphous dielectric materials such as silicon oxide and silicon nitride. Typically, a low power (500 W) radio-frequency (RF) discharge in a low pressure gas (0.1-1 torr) is used to produce free radicals and other reactive species, which then diffuse to the walls of the reactor and react to form a film. Since the discharge does not completely dissociate the gas, extensive surface reactions are required in order to give a dense, high quality, film and these are usually promoted by heating the substrate to 300-500°C. For example, a greatly simplified reaction scheme for the production of silicon nitride from precursors of silane and ammonia would be:



in the discharge, followed by



at the growing film surface.

Recent improvements in the PECVD technique include the separation of the discharge from the substrate and thus reliance on gas flow to

transport the reactive species[3] (Remote PECVD), magnetic enhancement of the discharge[4], and the use of the much higher frequency microwave discharge techniques[5]. These improvements are mainly aimed at avoiding the ion damage that has been shown to occur to sensitive CMOS integrated circuits exposed to a glow discharge[6] and, although important in this respect, do not overcome the main obstacle to applying the technique in many other fields; namely the requirement to heat the substrate to a comparatively high temperature in order to get a dense film.

This publication is the third in a series which describes a new plasma technique which overcomes this problem, and allows the deposition of good quality films at room temperature. This technique uses a high power ( $>300 \text{ Wcm}^{-3}$ ) discharge to completely dissociate the reactant gases to atoms, which then condense at the film surface. Since the reactant gases are atomised by the time they reach the substrate, no additional substrate heating is required to promote surface reactions. The discharge power is pulsed with the 'on' time sufficiently long ( $\approx 200 \mu\text{s}$ ) to provide the necessary degree of dissociation, and the 'off' time sufficiently long ( $\approx 40 \text{ ms}$ ) to keep the substrate temperature close to room temperature. In addition, the technique utilizes reactor geometries with a high gas conductivity which enable the gas composition to be varied between pulses and hence a very rapid variation of film types can be achieved.

In this publication, results on the use of the pulsed plasma deposition technique for the room temperature production of aluminium films and tin films are presented. Previously the technique has been used for the room temperature deposition of dielectrics[1] and compound amorphous semiconductors[2] from gaseous hydrides. These previous papers give extensive descriptions of the technique and present detailed comparison of films deposited by the pulsed plasma method and more conventional plasma methods. For depositing metals, volatile hydride precursors are not generally available and organometallic precursors have to be used instead; in this case trimethyl aluminium (TMA) and tetramethyl tin (TMT).

## EXPERIMENTAL

### Pulsed Plasma Equipment

Since the deposition plant has been described in detail elsewhere[1,2], only the relevant features will be given here. However, this work does make extensive use of the rapid changing of gas composition between RF pulses which, since this has only been briefly mentioned in the previous papers, will be discussed in more detail here.

The experimental rig is shown in figure 1. The generator

is controlled by the computer and gives short (100  $\mu$ s) pulses of RF power at up to 50 kW. Since the RF pulse rate is only 25 Hz the mean power into the chamber is of the order of 125 W, hence there is little heating effect on the substrate and the water cooling can keep the substrate temperature low. The substrate temperature was estimated on leaving the chamber as being  $<40^{\circ}\text{C}$ , and LCD temperature indication tapes placed on the substrate showed that the substrate temperature never exceeded  $60^{\circ}\text{C}$  during the deposition.

The flow of gases into the chamber is controlled by the computer via mass flow controllers, stop valves, and the pulsing valves. Due to the high capacity of the roots pump (about  $500 \text{ m}^3\text{h}^{-1}$ ), complete exchange of gases in the chamber can occur in less than 40 ms; this enables the chamber to be replenished with fresh gas between RF pulses. The mass flow controllers use heat transfer between a heater and a thermal detector as the basis of determining gas flow and require knowledge of the specific heat capacity of the gas in order to produce an absolute measurement of the flow. For the organometallics this is not an accurately known quantity, so in this paper, flows of the organometallic compounds are quoted as measured by the mass flow controllers when given the specific heat capacity of nitrogen. By comparison with the correction factors that have been quoted for other large molecules, the flows stated here are probably about four times larger than the actual flow of these compounds.

Trimethylaluminium and tetramethyl tin were chosen as the metal sources because of their relatively simple structures, containing only carbon and hydrogen as unwanted species. At the operating pressure (approximately 500 mtorr) the rate of evaporation of the TMA was high enough to maintain a steady flow of up to 50 sccm without the need for heating. To achieve greater flow required the use of the condenser as shown in figure 1. The heating of the TMA container increases the rate of evaporation of the liquid and the condenser controls the vapour pressure and prevents the hot vapour condensing in the cooler pipework leading to the chamber. Use of the heater combined with the condenser also allows the mass flow controller to be presented with a constant vapour pressure at its input despite 'bump boiling' of the TMA, and hence improves flow control. The TMT was much more volatile than the TMA and could be reliably controlled over a much larger range (up to 200 sccm). The use of this arrangement allowed much greater control and measurement than would have been possible using the more conventional bubbler techniques using carrier gases.

The gases used in the deposition were of electronic grade (>99.99%) and were transported to the chamber using helium leak tested stainless steel valves and argon arc welded stainless steel tubing. Great care was taken to purge the gas pipes before use to prevent air and other contamination getting into the system.



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Two types of RF electrode were used; a flat circular plate and a cup electrode, both 70 mm in diameter. The latter consists of a flange bored with a 23 mm deep hole into which the substrate is placed, and a lid with a 40 mm diameter hole. Both electrodes were made of copper and were water cooled. The flat electrode developed a d.c. self-sustained bias of 2000 V, whereas the cup electrode achieved a bias of less than 200 V at low partial pressures of argon, although this could be increased to 500 V by increasing the argon flow. The reason for the difference in the bias level as the reactor geometry was varied is not completely clear; it is believed it is only partly due to the difference in surface area of the electrodes, but is mainly caused by the discharge striking in a hollow-cathode type discharge in the centre of the cup hole. By using the two electrodes it was possible to see what effect bias and ion bombardment had on the film structure. In the case of tin deposition, substrates were also placed on the counter electrode which was connected to ground.

#### The Pulsing of the Gases

The pulsed plasma deposition plant can be operated in two ways. The simplest way is to keep the pulsing valves open all the time and use the mass flow controllers to alter the mixture of gases in the chamber. In this mode the process closely resembles conventional plasma deposition except that the discharge uses much higher powers and is pulsed. This is the method that was used in [1,2] in order to deposit dielectric materials and compound semiconductors. In this mode, it is only necessary to have sufficient flow of gas to allow the gas in the chamber to be exchanged between RF pulses.

A more versatile way to use the plant is to pulse the gas flows into the chamber. This has the major advantage that the gas type can be changed in a very short time such that each RF pulse sees a different gas composition. For reasons that are discussed in the next section, it was necessary to use the plant in this mode to obtain high quality metal films.

The pulsing of the gases is achieved using the pulsing valves shown in figure 1. These have been chosen for their fast operation ( $\approx 5$  ms), and consequently the principal delay in letting gas into the chamber is the finite conduction of the pipes in the manifold. The volume shown in figure 1 is pressurised when the pulsing valve is closed and the stored gas is released when the valve opens. This has two main advantages; firstly the mass flow controllers do not try to respond to the opening and closing of the gas pulsing valves, and secondly the pressure stored in the gas volume produces a pressure wave through the vacuum system when the pulsing valve opens. Since the conduction of a pipe increases with the pressure, this leads to a much faster exchange of gas in the reactor than would be possible without the volume.

Two methods were used to determine the effectiveness of the gas pulsing method in changing the gas in the deposition chamber. The simplest method is to place a microphone in the deposition chamber and record the passage of the pressure wave as the pulsing valve is opened. Figure 2 shows the passage of the pressure wave past a microphone with 25 kHz bandwidth placed on the RF electrode. These tests showed that the pressure wave reached the chamber in approximately 10 ms for a typical flow of 500 sccm. The pressure wave passes the chamber in a little under 15 ms, and consequently a stable pressure for the discharge pulse occurs 25 ms after the pulsing valves are energised.

To determine to what degree the gases are being exchanged between successive pulses requires the analysis of the gas composition in the chamber as a function of time. This was done by measuring the optical emission spectrum of the discharge as the time between the opening of the pulsing valve and the discharge pulse was varied. The optical spectra recording equipment consisted of a spectrometer/photomultiplier system and has been described previously[1]. The intensity of the emission lines was assumed to be proportional to the concentration of the emitting species in the gas.

The results of these tests showed that the worst gas exchange occurs when the flow of the pulsed gas, and hence the stored pressure in the volume, was kept low. Figure 3 shows the relative concentration of nitrogen as a function of time when nitrogen and argon are alternately pulsed into the chamber at 20 Hz, when the average chamber pressure was 170 mtorr and the average flow of argon was 500 sccm and the nitrogen flow was 1000 sccm. Greater than 93% of the nitrogen was removed from the chamber 50ms after turning the argon pulsing valves on, this figure rising to 97% after 72 ms. These times could be shortened by using higher gas flow rates or increased by using lower flow rates. For example, lowering the flows to 500 sccm of argon and 50 sccm of argon with an average chamber pressure of 100 mtorr reduced the gas exchange to 75% after 50 ms. Generally in this work the RF pulse was delayed with respect to the pulsing valve opening to ensure that the pressure wave had passed the chamber and that greater than 80% gas exchange had been achieved.

#### DEPOSITION WITHOUT GAS PULSING

Initial experiments used a gas mixture of TMA, argon, and hydrogen in the chamber without pulsing any of the gases, but this was found to produce low quality films which degraded immediately on exposure to air. SEM x-ray analysis and infrared spectroscopy revealed that the films had a high carbon content initially, but after a short exposure to air the carbon was replaced by oxygen. It is noted that bulk aluminium carbide reacts vigorously with moisture, producing methane and aluminium oxide.

Similarly, the films of tin produced from continuous flows of TMT, argon, and hydrogen were brown, soft, and had no metallic lustre, although they appeared stable in air. SEM x-ray analysis showed a large concentration of carbon in the films.

The origin of the carbon in the film is probably related to the surface chemistry at the plasma/film interface. In any case, for the room temperature deposition studied in this work, no conditions could be found which produce stable metal films using the discharge of a simple mixture of gases in the same manner as we have described for the production of films from hydride precursors in Part 1 and Part 2 of this series. However, it is interesting to note that attempts to make aluminium and tin oxides and sulphides from hydrides as described in part 2 for germanium compounds, have proved very successful with little or no carbon observed. Presumably this is due to the high volatility of carbon dioxide and carbon disulphide.

#### DEPOSITION WITH GAS PULSING

In order to get metal films, use was made of the pulsed gas concept where the gases in the discharge can be changed between RF pulses. The method used was that, after the carbide was deposited in the first RF pulse, the gas was changed to hydrogen and several RF pulses were used to remove the carbon as methane. Thus the technique used consisted of successive depositions of the carbide and subsequent etching of the carbon by hydrogen to leave the aluminium film.

The method by which the gases were pulsed into the chamber is described above. Each cycle of the process consisted of a pulse of TMA or TMT, argon, and hydrogen followed by a number of pulses of hydrogen with argon to remove the carbon as CH<sub>4</sub>.

#### Aluminium

Using the pulsed gases technique, stable aluminium films were produced on silicon and glass substrates. The quality of the films with varying numbers of hydrogen pulses was assessed using SEM x-ray analysis and resistance measurements. Typical deposition rates were 100-200 Å/minute.

Best results were obtained at a pressure of approximately 450 mtorr with a flow rate of TMA of nominally 20 sccm. The hydrogen and argon flows were 3450 sccm and 1000 sccm respectively. The high degree of computer control in the process allowed conditions to be different for each RF pulse. In particular the pulsewidth was increased from 100 µs to 500 µs together with a slightly higher power level for the hydrogen

pulses, to ensure complete dissociation. The hydrogen and argon flows were held constant in each pulse to avoid pressure fluctuations introducing instabilities into the plasma. Matching of the generator to the plasma was difficult since the changing gas composition resulted in a change of impedance; a compromise position was chosen such that none of the pulses caused instabilities in the discharge.

Figures 4 and 5 show the SEM x-ray emission profiles of films with two and twelve hydrogen etching pulses for each deposition pulse, recorded 24 hours after deposition such that all the carbon in the film had reacted with moisture in the air to form aluminium oxide. The apparent silicon content is due to the electron beam penetrating the film and into the substrate. All measurements were made with an incident beam energy of 8 keV. For comparison, standard samples of  $Al_2O_3$ , SiC and sputtered aluminium were run. The results obtained show a decreasing oxygen pick-up as the number of hydrogen pulses is increased with a stable film produced after a minimum of eight of these 'carbon clearing' pulses.

The resistance of the aluminium also decreased rapidly as the number of hydrogen pulses increased. Figure 6 shows the effect of the extra pulses on the sheet resistivity as measured using a four-point probe technique. The high values for the films with few hydrogen pulses were not very reproducible, presumably due to the reactive nature of the film. For comparison, the resistivity of a sputtered film deposited at about 250°C is also shown.

### Tin

When the substrate was placed onto the grounded electrode, the tin deposition showed similar behaviour to that observed for the aluminium, except that up to 25 hydrogen pulses for every TMT pulse were required to completely remove all the carbon impurity from the film. Possibly this can be attributed to the greater stability of tin carbide than the aluminium carbide, or possibly to the greater amount of carbon that can be included from the tetramethyl tin as opposed to the trimethyl aluminium. Typical deposition rates were about 100 Å/minute.

There were major differences in the deposition between the aluminium and tin when the substrate was placed onto the RF electrode and the d.c. bias was large. Using the flat electrode and a self-sustained bias of 2000 V during the pulse, all the films were found to be light brown in colour, hard, and were found to contain only carbon and no tin. Using the cup electrode and adjusting the flow of argon in the discharge to produce a low bias of less than 200 V, a metallic film could be produced using additional pulses of hydrogen in the same manner as when a substrate was placed onto the grounded electrode. However, when the flow of argon was higher and the bias exceeded about 400 V, no tin film could

be produced. Therefore control of substrate bias was critical in depositing a metallic tin film.

This observation tends to suggest that the net deposition of tin onto the RF electrode is the difference of the plasma-enhanced chemical vapour deposition and the physical sputter etching of material by the ion bombardment. With increased bias, the tin is preferentially sputtered, leaving only the carbon impurity behind. The aluminium is less affected, presumably due to its lower sputtering yield. Published figures for sputtering yields appear to confirm this; the ratio of argon sputtering rates of C:Al:Sn being quoted[7] as 40:640:1217 A/minute.

#### DISCUSSION

Aluminium is widely used for interconnection between circuits in integrated circuits, as an electrode material in passive devices such as quartz resonators, and as a reflective element in optical storage media such as optical discs. In contrast, the comparatively poor conductivity and chemical stability of tin has led to few uses as a thin film material.

Conventionally, metals are deposited onto the surface of a substrate by evaporation or by sputtering (for a review see [8]), although other methods have been suggested such as chemical vapour deposition[9], plasma-enhanced chemical vapour deposition[10] and laser-induced chemical vapour deposition[11]. Good criteria for the quality of the coating is its conductivity, adhesion to the substrate, and the degree to which the films corrode in moist environments.

The electrical conductivity of aluminium is well known to be a function of both impurities and grain formation in the film. Sputtering and evaporation allow the purity of the aluminium to be closely controlled and provided the pressure is kept low enough to prevent gas inclusion into the film, high purity aluminium can be deposited. Grain formation in the film can be a problem at low temperatures, and generally substrates are heated to encourage greater atom mobility and the deposition of a uniform film. Chemical vapour deposition techniques generally produce films of lower purity due to inclusion of carbon and hydrogen from the source material, although deposition carried out at temperatures  $>300^{\circ}\text{C}$  have produced films of greater than 99.9% purity[9]. The pulsed plasma deposited aluminium has been purified by subsequent hydrogen pulses to give a film of greater than 98% aluminium while keeping the substrate at room temperature. No grain formation in the film has been found to occur if the deposition rate is kept low (i.e. the partial pressure of the TMA is not too high). Consequently we suspect that the difference in conductivity between the best room temperature deposited pulsed plasma films and the  $250^{\circ}\text{C}$  sputtered film is the result of residual carbon still remaining in the film, despite the hydrogen etching.

Adhesion of sputtered and evaporated metal films to silicon substrates has been widely discussed in the literature. The adhesion can be improved by adhesion promoters and this effect has been used to improve the adhesion of thermal chemical vapour-deposited aluminium layers[9]. Adhesion of pulsed plasma deposited films in general has been shown to be high[1], although more quantitative work on a variety of substrates will need to be done to confirm this.

Corrosion of deposited aluminium films is important industrially since it is known to be a major source of integrated circuit failure[13]. Further work is underway on the pulsed plasma films in order to test their response to adverse environments, but preliminary results indicate no appreciable change in conductivity or appearance on heating in air at 300°C for one hour or immersion in water for periods of a week.

Although unlikely to displace sputtering and evaporation as the standard method for depositing metallic films, the method could be used to advantage where low temperatures and the need to produce an adherent interface to a difficult substrate is important. An important advantage of this method over others could be the ability to deposit one or more adhesion layers between substrate and film and hence reduce stresses and improve adhesion. One such area could be the metallization of plastic disks used as optical storage media.

#### CONCLUSIONS

This paper has introduced a novel adaptation of the pulsed plasma deposition technique; namely the use of etching pulses to remove unwanted material from a depositing film. For organometallics, hydrogen can be used to remove carbon residues from the film and we have demonstrated that moderately high purity aluminium and tin can be made using this method.

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LEGENDS FOR FIGURES

Figure 1: Schematic of deposition equipment.

Figure 2: Pressure wave of gas passing through the deposition chamber as the pulsing valves are opened.

Figure 3: Emission of light from  $N_2(B^3\pi$  to  $A^3\Sigma)$  from the discharge as the pulsing valves are operated. For conditions see text.

Figure 4: Aluminium deposited from an Ar, H<sub>2</sub>, and TMA pulse and then followed by two H<sub>2</sub> pulses onto a silicon substrate.

Figure 5: Aluminium deposited from an Ar, H<sub>2</sub>, and TMA pulse and then followed by twelve H<sub>2</sub> pulses onto a silicon substrate.

Figure 6: Variation of the resistivity of the aluminium as the number of H<sub>2</sub> pulses are varied. For comparison, the dashed line shows the resistivity of a sputtered film deposited in a commercial magnetron sputtering plant at 250 °C.

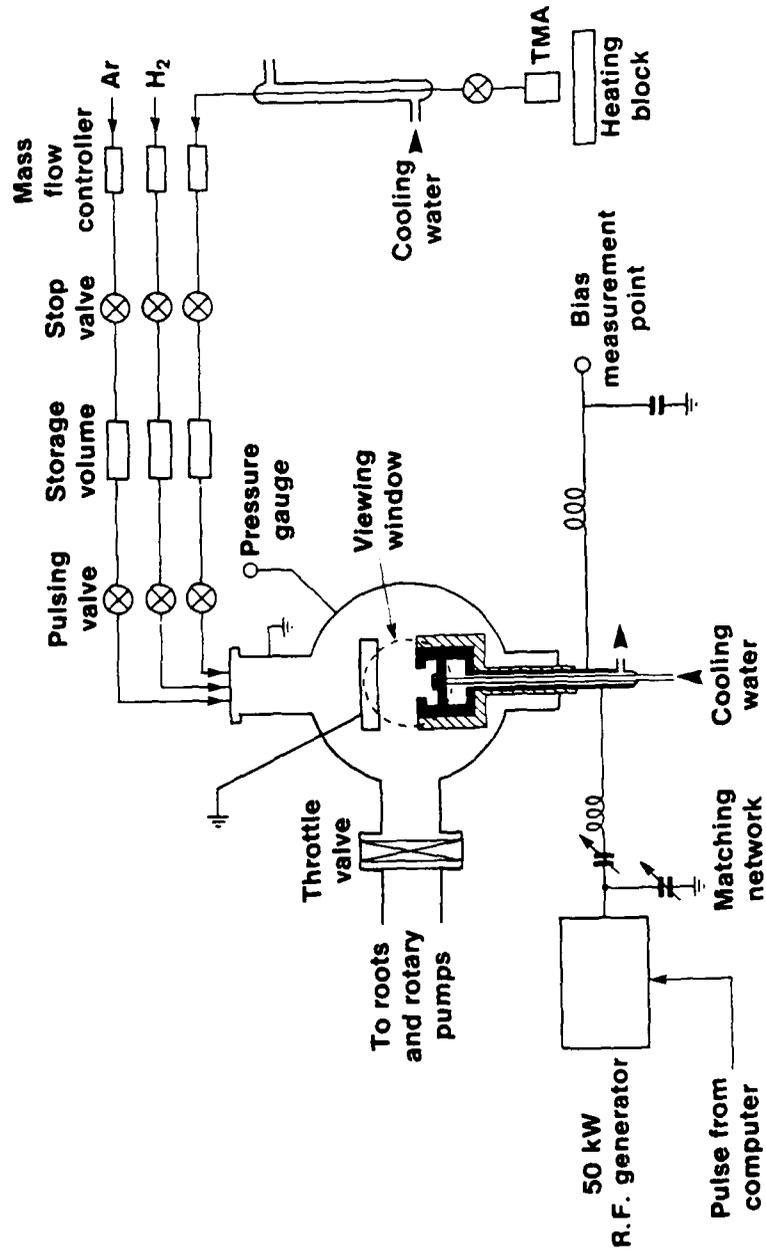


Fig. 1

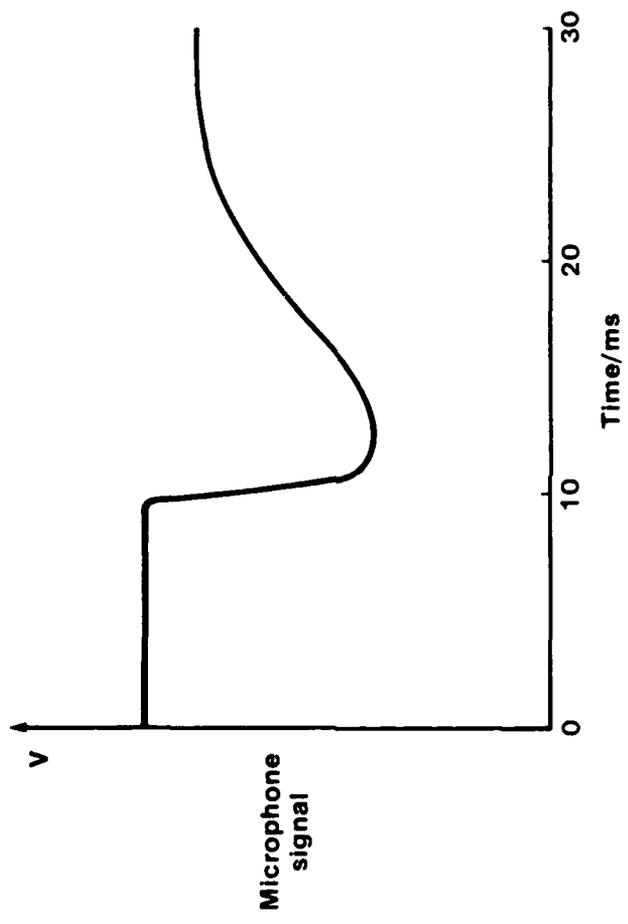


Fig.2

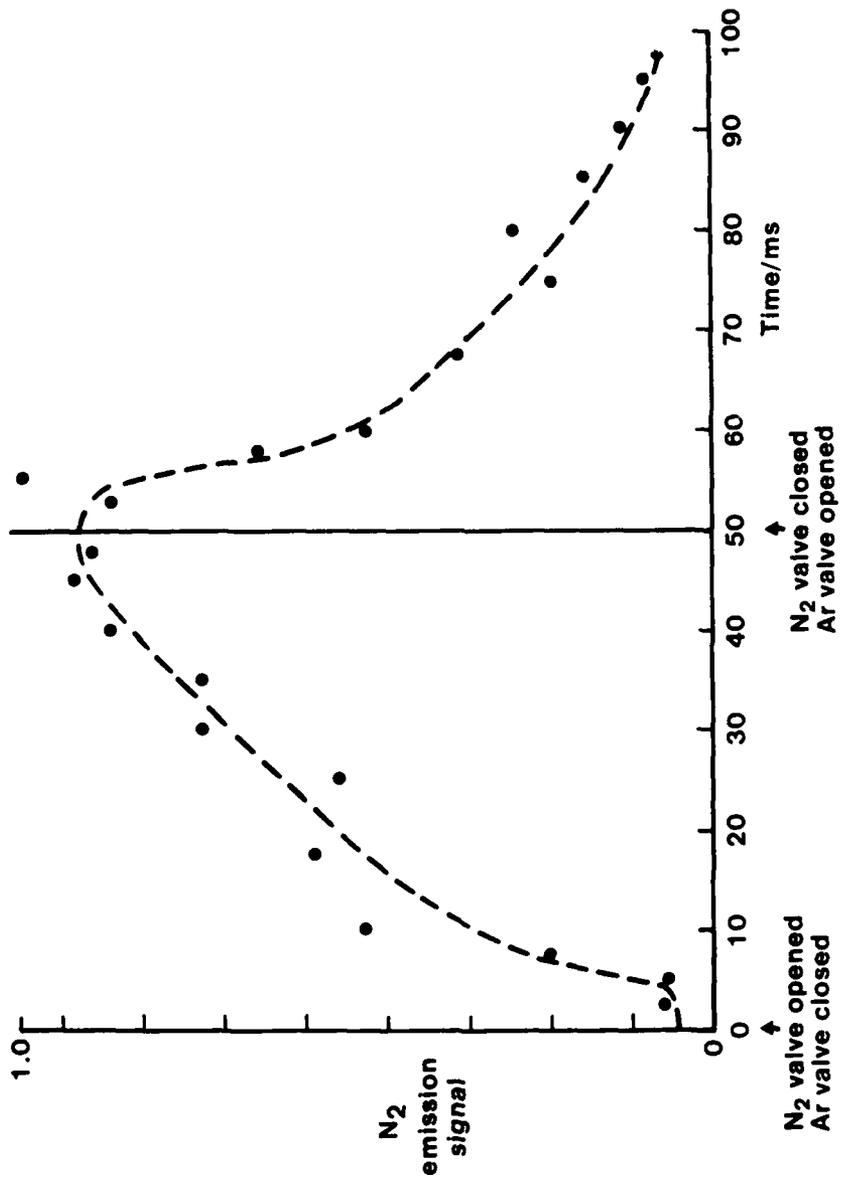


Fig. 3

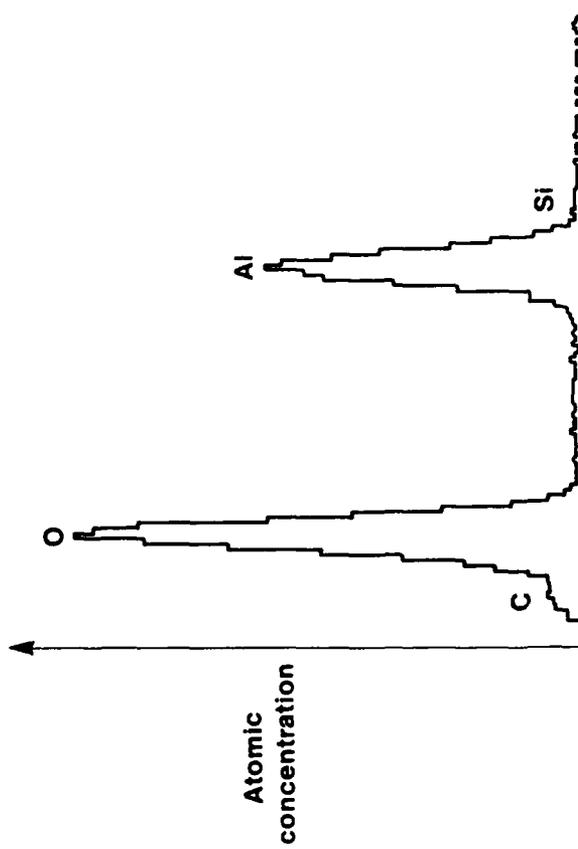


Fig. 4

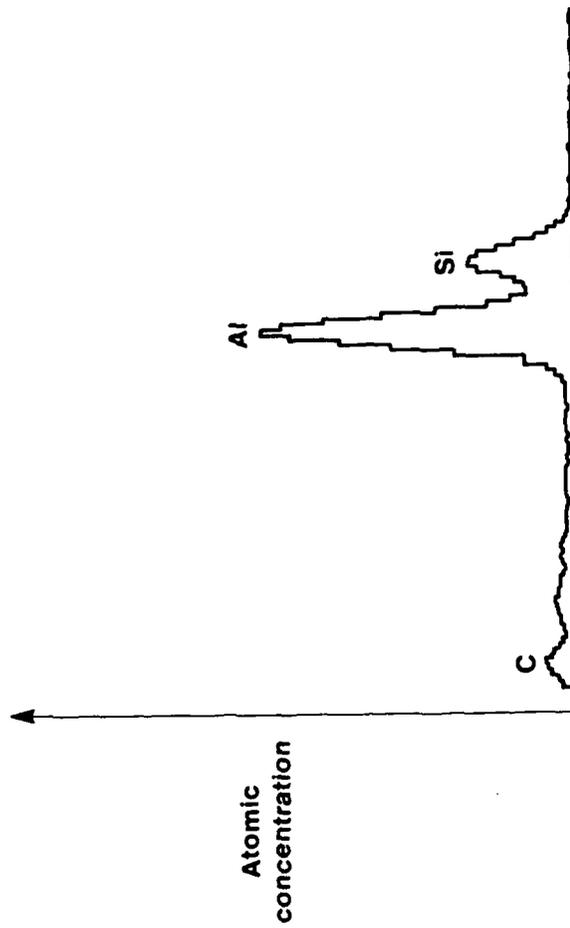


Fig.5

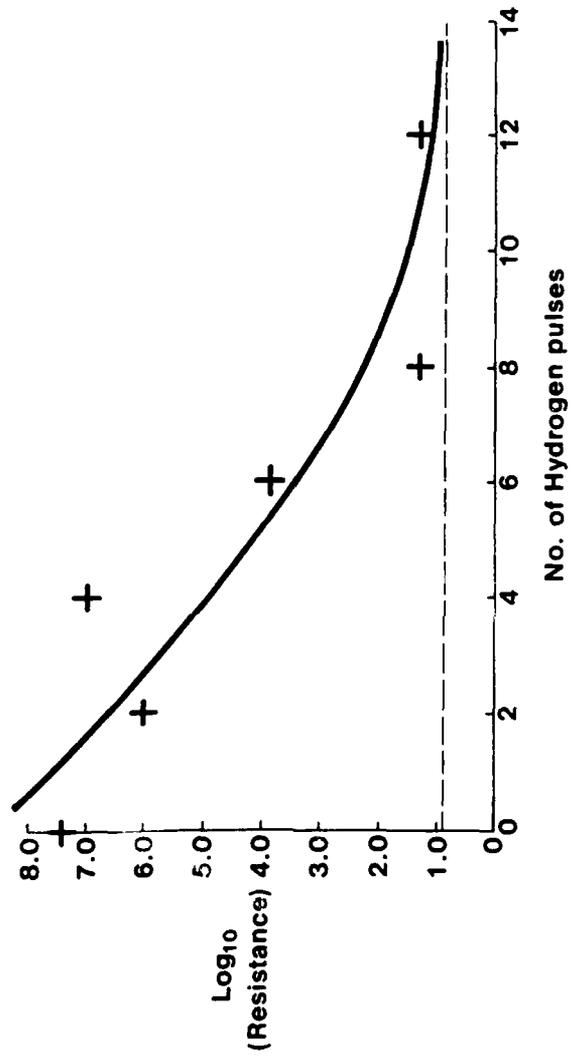


Fig. 6